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EELS Monitoring of Beam-Induced Dynamic Transformation of Lithium Materials at 30 keV

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Lithium-ion battery are now ubiquitous in every part of modern life; from electric cars and laptops to USB rechargeable bicycle lights. In all these applications, a common failure mode is the degradation of battery storage capacity. Understanding the nature of battery degradation mechanism is the first step toward making longer-lasting batteries. A scanning transmission electron microscope (STEM), equipped with an electron energy loss spectrometer (EELS), is used here to investigate battery materials, since such equipment has both the spatial resolution to image nanostructures and the spectrometric capabilities to identify lithium species [1]. In some of our recent work using TEM on battery materials has shown sodium enrichment on the surface of $FePO_4$ anodes [2] as well as enabled the characterization of polymer coating on $Li_4Ti_5O_{12}$ anodes [3]. Here we report advances in characterizing the beam-induced transformation of three lithium-based materials.

High energy beam can create substantial specimen damage [4], [5]. It is therefore critical to understand how lithium behaves when irradiated by the electron beam. The two main damage mechanisms are ionization (radiolysis) and atomic displacement (knock-on damage). Radiolysis is generally described as the breaking of chemical bonds due to ionization of the bonding electrons. The radiolysis can manifest itself with the generation of new chemical species in situ [1]. Such generation is reported here in the study of lithium fluoride. Knock-on damage is due to momentum transfer during an electron-atom collision. In most cases the atomic displacement cross-section increases as the beam energy decreases, until the beam falls below the atomic displacement threshold for a given material. Knock-on damage can be avoided if the beam energy is lower than the displacement energy [5]. In the case of lithium, however, the Mott model suggests an increased displacement cross-section for knock-on damage at low energies [6].

Thus, a 30 keV cold-field emission STEM-EELS instrument, the Hitachi SU9000EA is used. This instrument working energy may exacerbate the transformation mechanisms. The microscope has an estimated probe size of less than 0.5 nm and an energy beam resolution 0.55 eV [7]. Several commercially available lithium compounds were purchased from MilliporeSigma and were inspected in the microscope. EELS time series were collected. Figure 1 shows the beam-induced transformation of three materials: lithium fluoride, lithium chloride, and lithium carbonate. The beam-induced transformations are observed in both the low-loss region as well as in the fine structure of the lithium K-edge. A common trait for the three datasets is loss of mass of the sample. This mass loss reduces the thickness over mean free path ratio (t/λ). The effect of this shift in t/λ is most visible in the low-loss series of LiCl, where the intensity of the signal increases to the point of saturating the detector. The LiF time series shows a transformation from LiF to lithium metal. The Li_2CO_3 low-loss series shows a gradual splitting of a peak at 10 eV, also indicating a change in the chemical nature of the material.

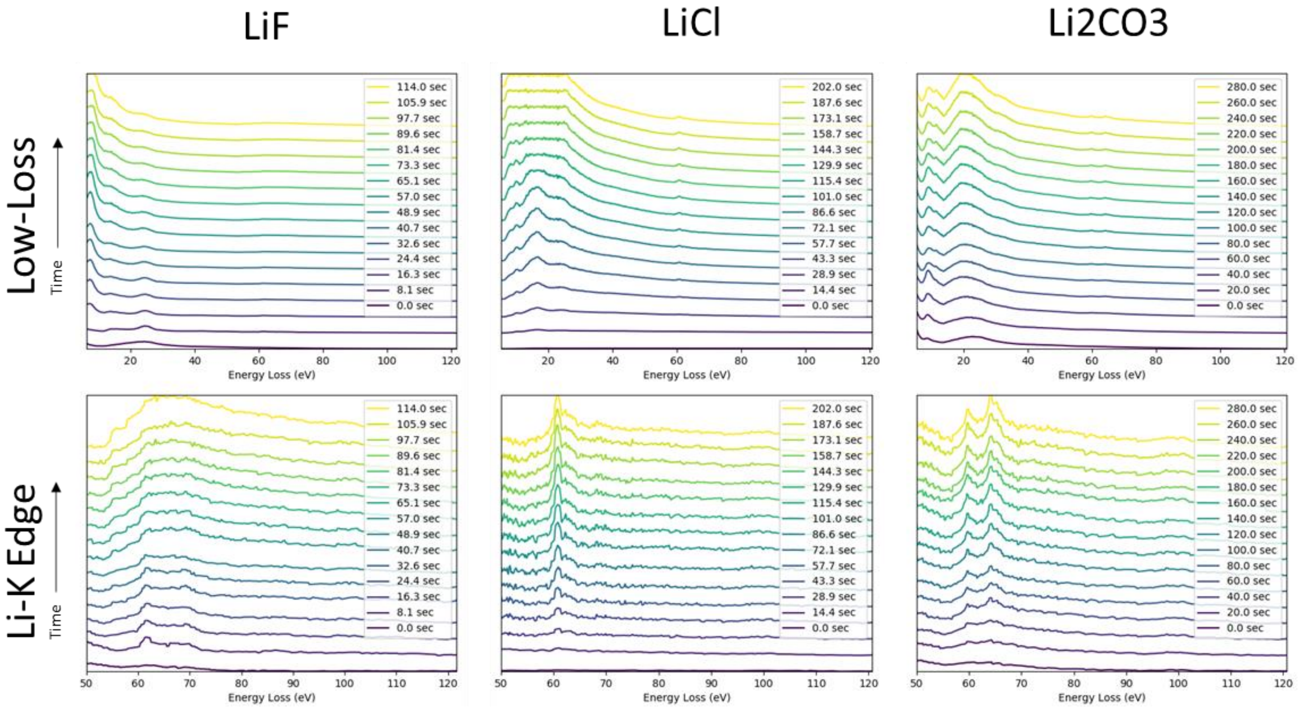

Figure 1. EELS time series of lithium fluoride (LiF), lithium chloride (LiCl), and lithium carbonate (Li2CO3). The spectra are acquired with an incident beam energy of 30 keV, in the 3 to 120 eV range (upper panels). A background subtracted intensity of the lithium K-edge is shown on the lower panels. The three materials exhibit significant beam-induced transformations.

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